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MOLECULAR BEAM SAMPLING MASS SPECTROMETRY OF HIGH
HEATING RATE PYROLYSIS: DESCRIPTION OF DATA
ACQUISITION SYSTEM AND PYROLYSIS OF HMX IN A
POLYURETHANE BINDER

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March 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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The data acquisition capability of the time-of-flight mass spectrometer used with the molecular beam sampling system has been expanded. An oscilloscope intensity-modulated raster technique using negative film scanned by a microdensitometer provides simultaneous semi-quantitative time-resolved mass spectra of all masses up to 160 amu with time resolution down to 10 ms. A system of parallel sample/hold channels which follow predetermined masses with time resolution near that of the spectrometer cycle time has been assembled and

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shown to have good dynamic range, adequate mass resolution, and provide good reproducibility. This system has been used to study the products of low pressure pyrolysis of nitrocellulose and cyclotetramethylene tetranitramine/polyurethane binder. Using a carbon dioxide laser for heating the samples up to 5000 deg/s heating rate effects are clearly demonstrated for NC but are not observed for HMX/PU. Relative amounts of the major decomposition species observed for the HMX/PU were nitrous oxide, 100; nitrogen dioxide, 54; hydrogen cyanide, 42; formaldehyde, 39; and nitric oxide, 27. The large amounts of nitrogen dioxide is compatible with the breaking of the N-N bond as the first step of the thermal decomposition of HMX.

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I. INTRODUCTION

The detection and concentration measurement of the chemical species present in the ignition and combustion of propellants and related materials is a basic input to computer models which hold the potential of rational design of propellants to optimize necessary performance parameters. The method used in the work described here consists of extracting a sample of the gases from the process of interest by expanding it through a supersonic nozzle which forms the species into a molecular beam. The molecular beam is characterized by low vibrational and rotational temperatures and a narrow velocity distribution which result in the quenching of further chemical reactions. The sampled species are then ionized by impact with low energy electrons (10 to 70 eV) and the resultant ions analyzed by a mass spectrometer. This technique has been used successfully by many previous investigators[1] to study both stable and highly reactive species. The design details of the apparatus used in our laboratory studies have been described in detail elsewhere[2].

The choice of a time-of-flight mass spectrometer for our applications yields the time response required, but also results in difficulties in recording the data due to the high rate at which information is presented. In this report traditional recording methods and new methods developed for our studies are described in detail. Preliminary results from studies of low pressure pyrolysis of some propellant materials at high heating rates are presented and the meaning of these data discussed.

II. EXPERIMENTAL

The time-of-flight mass spectrometer (TOFMS) is a simple device for analyzing the mass-to-charge (m/e) ratio of a collection of ions, either extracted from some physical process or created by impact of a short pulse of low energy electrons on a gas of molecules or atoms.

[1] a. J. W. Hastie, "Sampling Reactive Species From Flames by Mass Spectrometry", Int. J. of Mass. Spectry. and Ions Physics, 16, 89-100 (1975).

b. R. V. Serauskas, G. R. Brown, and R. Pertel, "A Supersonic Molecular Beam Atmospheric Pressure Flame Sampling System", Int. J. of Mass Spectry and Ion Physics, 16, 69-87 (1975).

c. J. C. Biordi, C. P. Lazzara, and J. F. Papp", "Flame-Structure Studies of CF_3Br-Inhibited Methane Flames", Symp. (Int.) Comb. (Proc.), 14th, 367 (1973).

[2] K. J. White and R. W. Reynolds, "Apparatus for Detecting Interior Ballistic Combustion Products", BRL Memorandum Report No. 2497, AD #AO13372 (1975).

The ions are accelerated to a kinetic energy of typically 2 KeV. Since all ions have the same energy, the lighter have higher velocities and therefore arrive at the detector in shorter time. In our configuration, the ions with m/e from one to 160 amu/charge arrive at the signal anode within 10 μs with each m/e peak 10 to 20 ns wide. If no masses greater than 160 amu are expected one may repeat this cycle at 100 KHz and obtain a complete mass spectrum each 10 μs. Since these signals require at least 30 MHz bandwidth for recording, conventional analog magnetic tape is too slow; faster methods are limited by ability to store the quantities of information generated. The alternative methods of recording the mass spectra are discussed below.

In studying phenomena which vary on time scales near the 10 μs spacing of spectra from the TOFMS, recording oscilloscope traces of the spectra photographically is a useful method of data acquisition. The use of vertical and horizontal offsets allows the recording of multiple spectra with one picture; high speed cameras can be used for recording spectra over longer time periods. The principal difficulties associated with this technique include the effort involved with extracting numerical values from pictures, unsatisfactory signal averaging techniques such as multiple exposures of spectra, and the large quantities of data involved with events occurring over time periods of milliseconds or longer.

The analog recorder is the second commercially available option, and the one most commonly used for studies of steady state phenomena where one may leisurely scan the mass spectrum or in time dependent phenomena where information from one mass will be adequate. In this system, a fast voltage pulse gates the electrons resulting from a single mass onto a separate anode near the end of the electron multiplier. This current is then amplified by an electrometer with risetime as fast as 1 ms, resulting in a well-behaved easily-recorded signal. By using a variable delay with the gate pulse one may select masses sampled or sweep the mass spectrum at an appropriate rate.

The analog recorder is limited in versatility by the restriction in the number of masses which can be followed in time; systems of up to four gates are possible with some effort. A major disadvantage is that the gate pulses distort the mass spectrum signal and thus make simultaneous observation of the entire mass spectrum very difficult. The limitations imposed by the electrometer time response may be important in very fast studies.

The Oscilloscope Intensity-Modulated Raster technique was first reported[3] a number of years ago as useful for making qualitative records. Figure 1 shows a block diagram for this method. If one

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[3] K. A. Lincoln, "Simple Display System for Recording Time-Resolved Mass Spectra", Rev. Sci. Instr., 35, 1688 (1964).
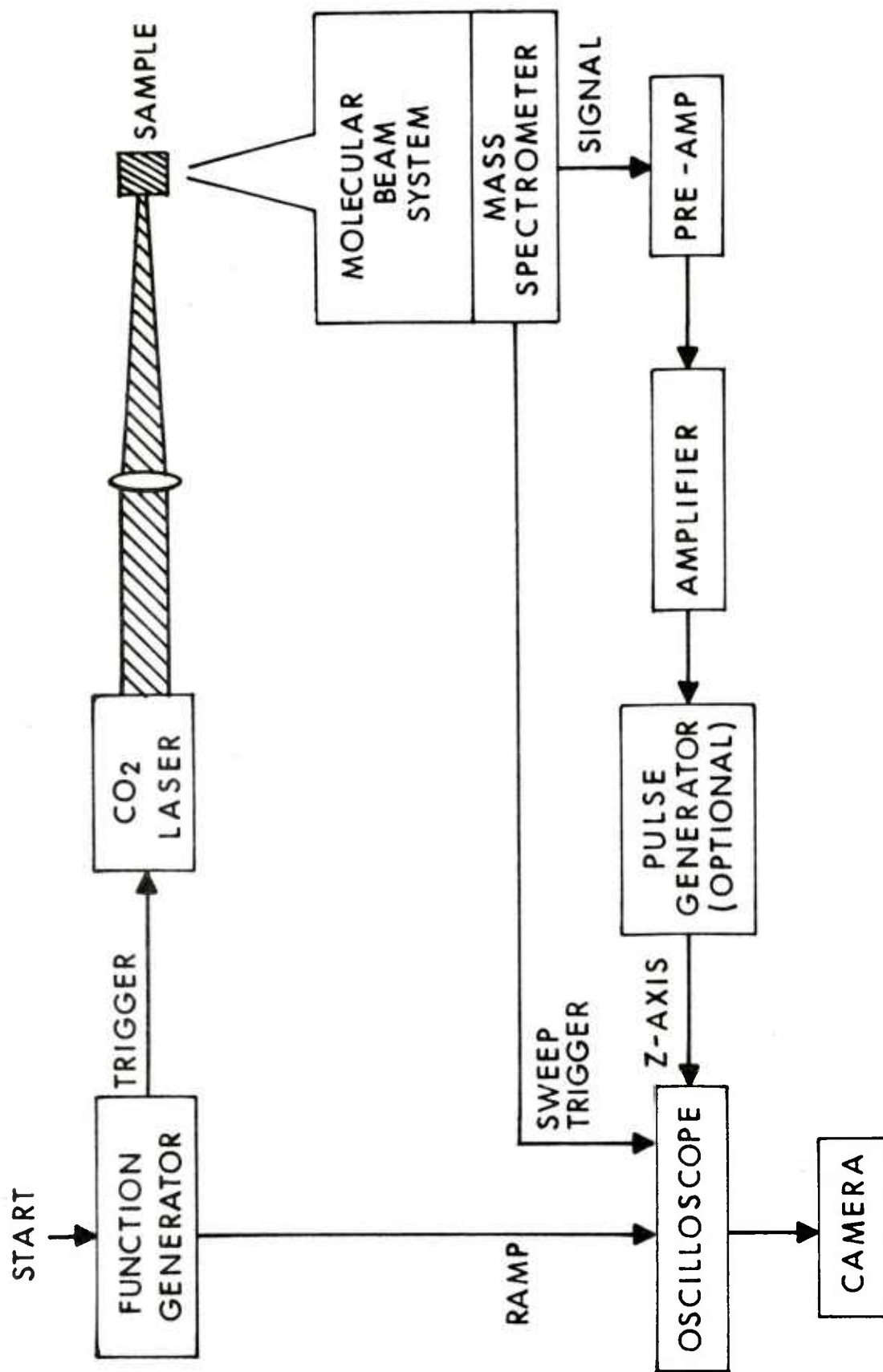
Figure 1. Block Diagram for Oscilloscope Intensity-Modulated Raster Recording Technique

suitably amplifies the pulses which make up the mass spectrum they may
be used to modulate the intensity of an oscilloscope. If that trace is
adjusted to the point where no trace is visible when no mass is de-
tected, the oscilloscope displays a series of dots with position
identifying the mass and intensity the relative signal strength. A
ramp is then used to move the successive spectra up the oscilloscope
screen during the event being measured. The result is a three-dimen-
sional display of the complete mass spectrum as a function of time.
Use of a fast film such as type 107 Polaroid yields a good qualitative
record of the event. A major improvement was made in our capability by
using type 665 positive/negative film. With either film, good results
are obtained for scans as short as 100 ms with time resolution of
approximately 10 ms. However, with the negative one may use a micro-
densitometer to convert the data to graphic or numerical form. Figure
2 shows a smoothed plot from a microdensitometer scan of NC pyrolysis
at low pressures.

The most serious disadvantages of this method are that the system
appears to have a limited dynamic range as well as a potential threshold
below which masses are not detected. It is also quite difficult to pro-
vide a good calibration for absolute concentration measurements of
species. However, this method can provide a good survey of masses
evolving during a process, help in identification of chemical species
through peak height ratios, and provide good quantitative information
where absolute concentrations are not important.

As mentioned earlier, magnetic recorders do not have the bandwidth
necessary to record the TOFMS signal directly to make use of their good
memory size. Solid state transient recorders are available with
sufficient bandwidth but are of limited memory size. It would take at
least 2 ms to dump the memory of a typical transient recorder into a
microprocessor or other device after recording 20 μs of data. This
deadtime is quite undesirable since the averaging of several adjacent
mass spectra without loss of time resolution is essential for good
signal-to-noise ratios. Attempts have been made to use two transient
records to eliminate storage when no mass peaks are present. The first
recorder is turned on electronically whenever a mass peak is present
and records the peak; the second recorder is used to mark the times and
therefore identify the masses. In this manner, the amount of recorded
information between memory dumps would be greatly increased. A micro-
processor or other device could then be used to reconstruct the mass
spectra as a function of time. Unfortunately, in preliminary trials
of this technique it proved unreliable, although it possibly could be
made to work if more attention were paid to quality of switching
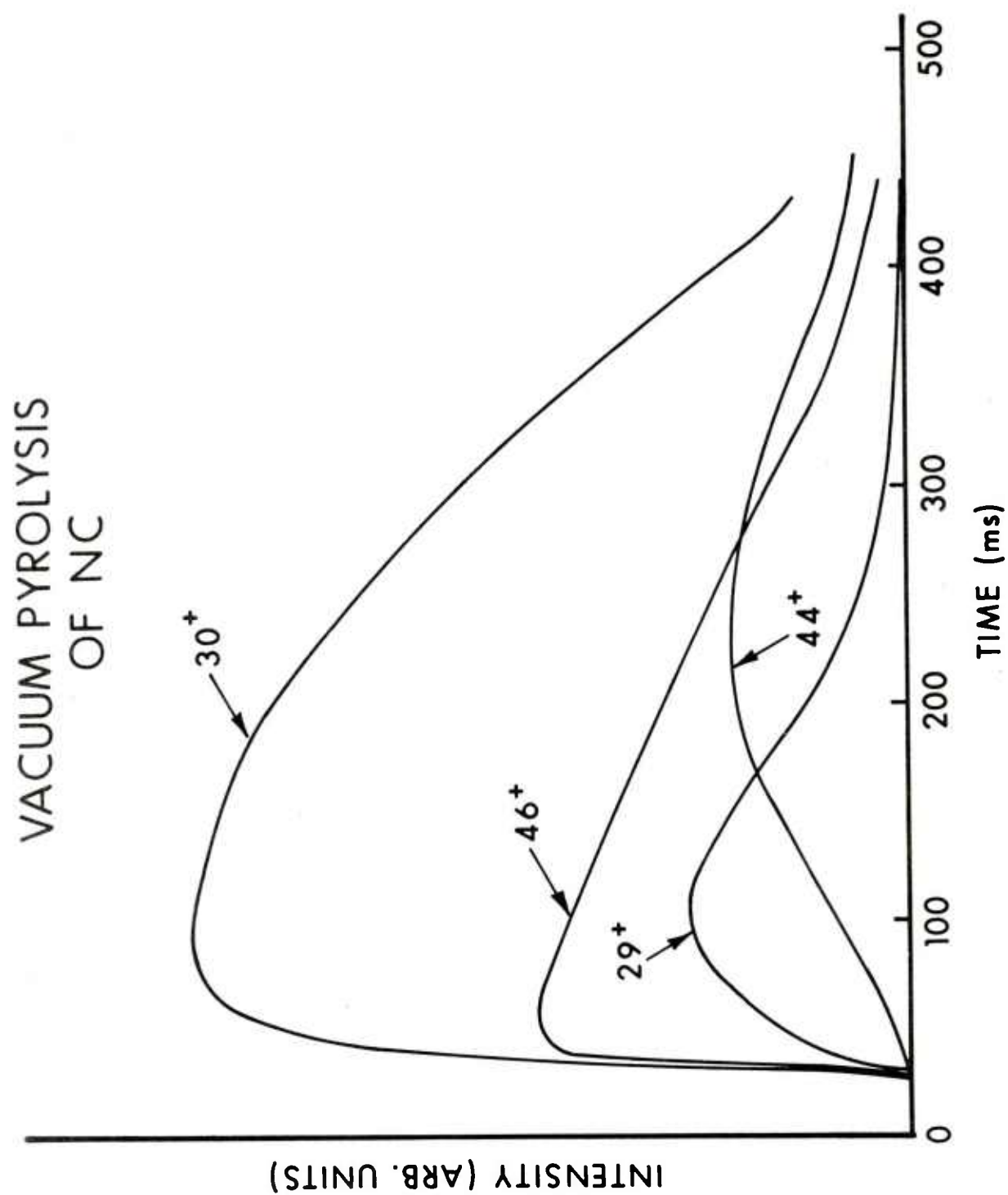pulses, and other details.

Figure 2. Temporal Behavior of Four Selected Mass/Charge Peaks During and After Rapid Pyrolysis of NC

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The next most desirable option is a system of parallel channels each of which could follow a pre-selected mass without limiting the time resolution. In order to maximize the signal-to-noise without decrease in the already limited duty cycle of the mass spectrometer, the ideal gate element of such a system should integrate the mass peak over its limits and provide an output without major reduction in the 100 KHz rate of the spectrometer. Good charge digitizers take about 20 μs to digitize data with further time required for storage of the data. Available non-digital devices are designed to give out a pulse proportional to the area integrated; the time required for pulse height analysis again is substantial.

Another possibility using commercial integrated circuit components is to have a wide-band sample/hold module for each of the masses to be measured. The sample/hold is a simple device which follows the analog signal until its logic command is switched; it then acquires the signal voltage and maintains an output at that level until the logic command is reset. Although some sacrifice in signal-to-noise is made in using only the peak rather than the entire area, these circuits have been found to provide good dynamic range with reproducible operation and are readily calibrated. For this work a model 1024 from Optical Electronics Inc. was utilized in each circuit. These modules were selected primarily on the basis of their 30 MHz tracking bandwidth and 3 ns aperture time. The amount of jitter in the gate generator providing the logic pulse is the major limitation in mass resolution. Standard solid state pulse and gate generators from three different manufacturers were found to give mass resolution similar to that of Figure 3. Use of digital delay generators and 100 MHz bandwidth devices should result in mass resolution equal to that of the mass spectrometer. The time resolution is in principal the cycle time of the mass spectrometer, although in practice one would usually prefer to sacrifice some time resolution to increase the signal-to-noise ratio. There are currently four parallel circuits in use with this apparatus; the number of channels can be expanded arbitrarily for approximately $1K per channel, up to the limit of the recording device. The system is designed for either analog tape recording of the channels output or direct digitization by a computer. For the preliminary studies reported here, the outputs have been recorded by a four-channel storage oscilloscope.

III. LOW PRESSURE PYROLYSIS STUDIES

In order to apply our system to the study of early thermal decomposition species of energetic materials, a small vacuum chamber was mounted around the sampling area with provisions for mounting a sample of the material of interest near the sampling nozzle. The heat source used in these studies was a nominal 50W CO_2 laser which was directed unfocused onto the sample through a NaCl window on the vacuum pyrolysis chamber. Although no temperature measurements were made, estimates of the heating rate based on delay from start of heating to arrival of products yield values near 5000 deg/s. Pumping of the chamber was pro-
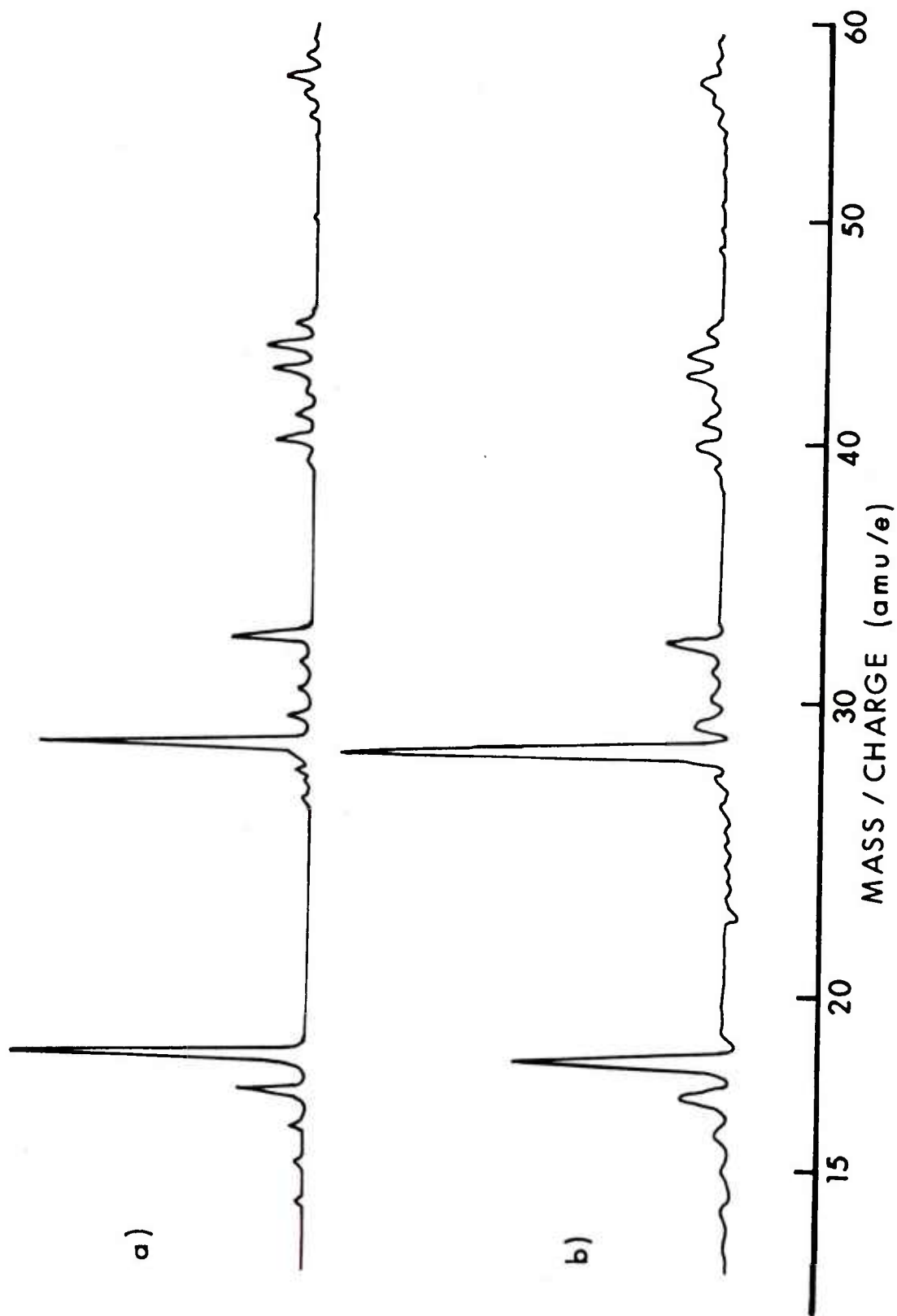
Figure 3. Typical Results of Slow Scans of the Background Mass Spectrum Showing Resolution of (a) The Analog Scanner System, and (b) A Sample/Hold Channel

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vided solely by the 2.5 mm diameter nozzle. Pressures were monitored by a capacitance manometer; typical background pressures were a few mTorr or less with peak pressures varying up to several hundred mTorr. The geometry is such that the early signals should be dominated by species which have left the heated surface and are sampled without experiencing wall collisions.

Previous studies of the pyrolysis of nitrocellulose have indicated the presence of such final product molecules as CO_2 and H_2O which appear to result directly from the pyrolysis. In slow heating experiments, one may postulate that these species are the results of reactions in the solid phase involving primary decomposition species which are trapped within the volume and therefore not pumped away even though the nominal pressure remains very low. If one increases the heating rate to accelerate the pyrolysis process and eliminate the problem of solid phase reactions one may quickly reach a circumstance where decomposition product generation is so rapid that even unlimited pumping speed might not prevent the reaction of the highly reactive species as they leave the heated sample. Through the addition of time resolution to these studies, one may potentially detect any such difficulties and perhaps extract data on the nature of the primary decomposition species and subsequent reactions among them.

In order to verify that our technique could readily detect effects such as described above, a series of pyrolyses was performed on nitro-cellulose (NC) and cyclotetramethylene tetranitramine in a polyurethane binder (HMX/PU). As only semi-quantitative data were sufficient for these studies, recording was with the oscilloscope raster technique and microdensitometer tracing of the resultant negatives. For rapid heating of NC a 100 ms pulse from the laser typically produces behavior such as in Figure 2. The less than 1 mg sample is completely consumed before the end of the laser pulse. It is quite clear that CO_2 (mass peak 44) is a result of gas phase reactions. The other peaks recorded in this figure are from NO_2 (46 and 30), NO (30), HCHO (30 and 29), and possibly other aldehydes contributing to the 29 peak. If one reduces the laser power to near 15W and uses a thin film of NC a slower pyrolysis can be achieved. The results of a typical event can be seen in Figure 4. Even though this event is fast compared with traditional slow temperature controlled thermal decomposition, the effect of solid phase chemistry is seen clearly in the relative enhancement of CO_2 in the second peak near 1.8s.

The results of typical traces of similar experiments on HMX/PU (3:1; 5μ HMX particle size) are shown in Figures 5 and 6. In the slower pyrolyses there generally appears to be no change in the relative intensities of masses 27, 29, 30, 44, and 46 with the exception of a decrease in mass 46 under conditions where it may be lost to reaction with HCHO. The faster, higher power laser pulse heating in some cases shows a second peak of 44, which has been identified as CO_2 by the appearance of CO_2^{++} at 22 amu/e at corresponding times. This species

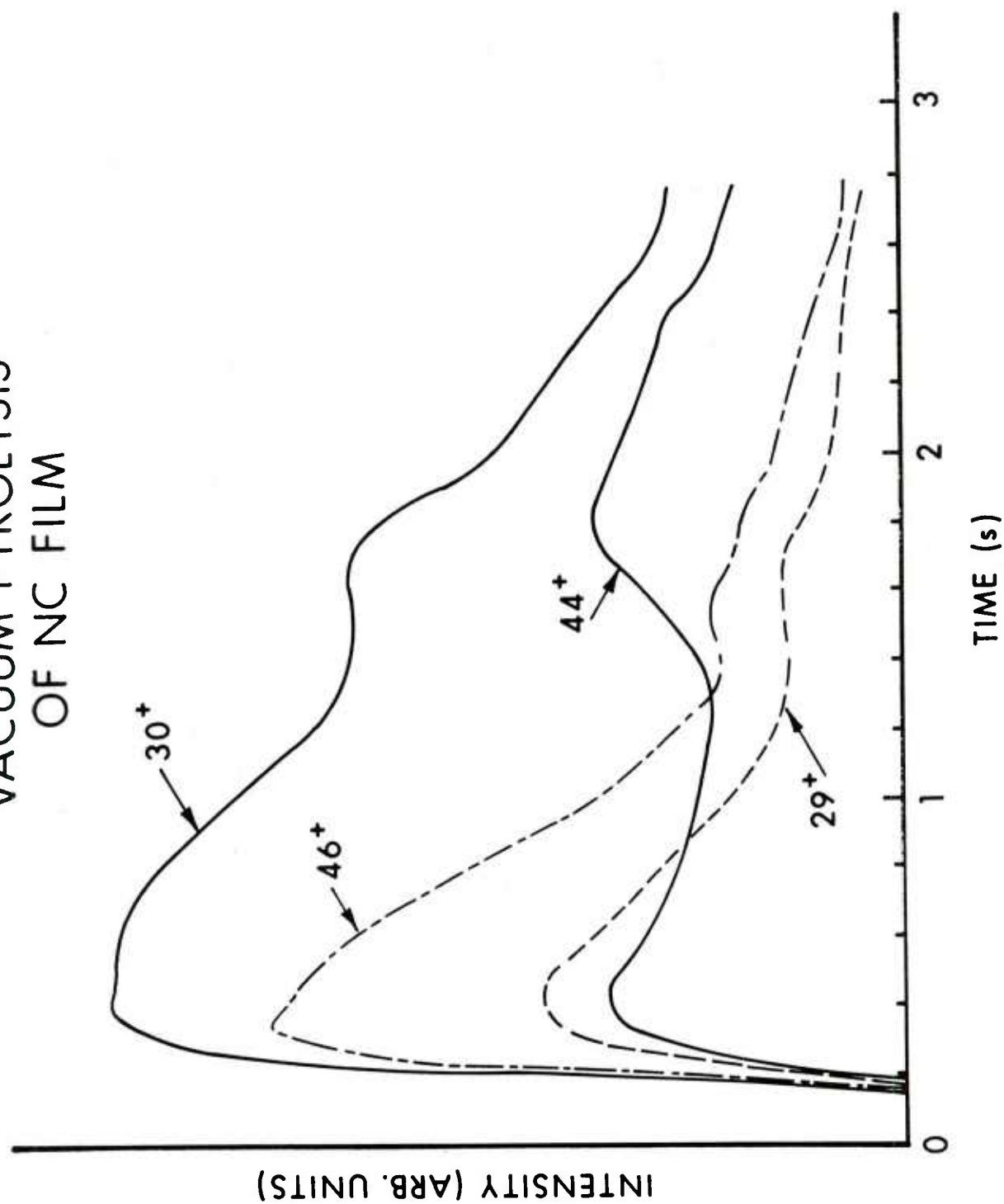Figure 4. Slow Time-Resolved Pyrolysis of 0.5 micron NC Film

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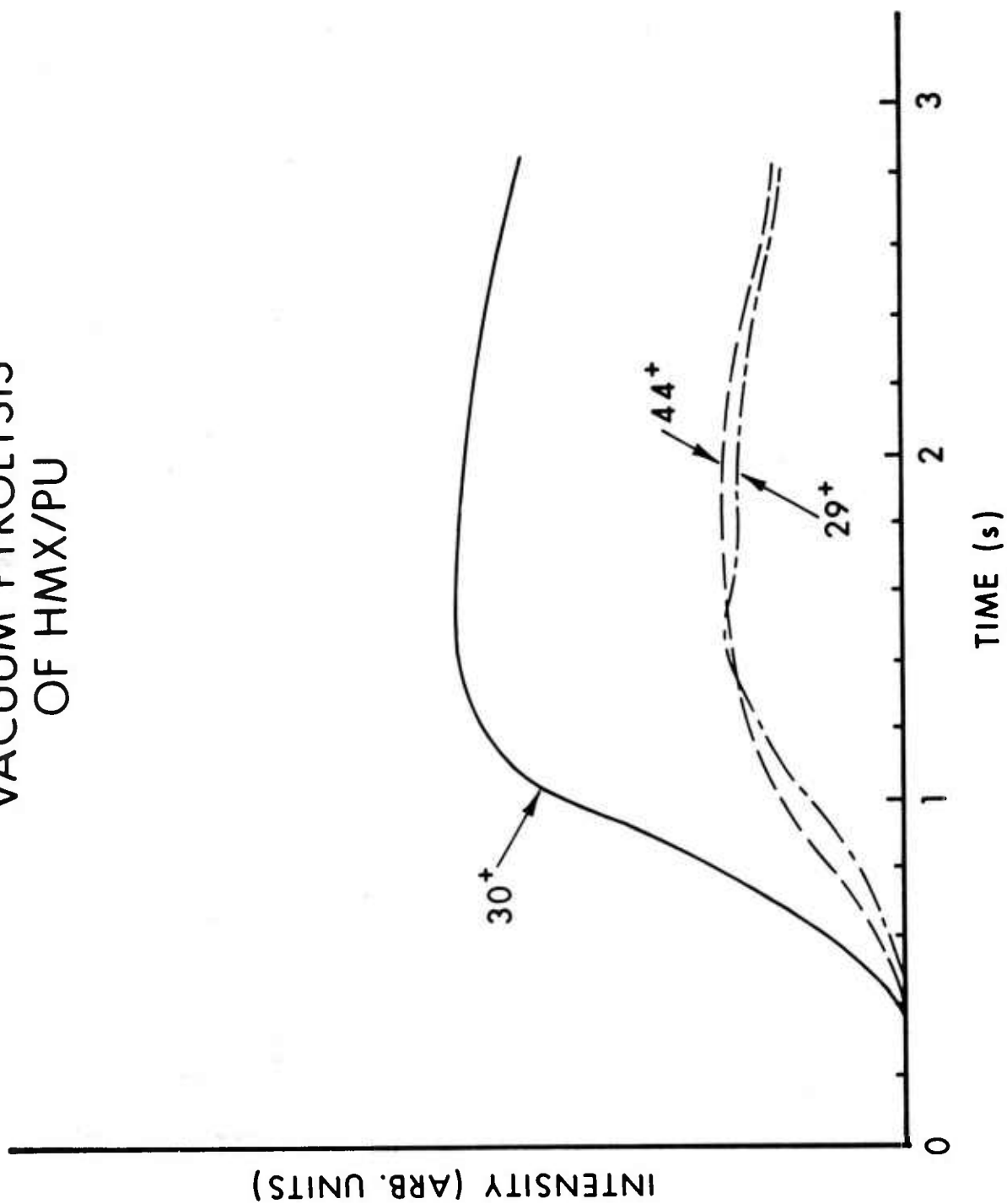
Figure 5. Slow Time-Resolved Pyrolysis of HMX/PU. Sources of Observed Masses are N_2O (44) HCHO (30 and 29), and NO and NO_2 (30)
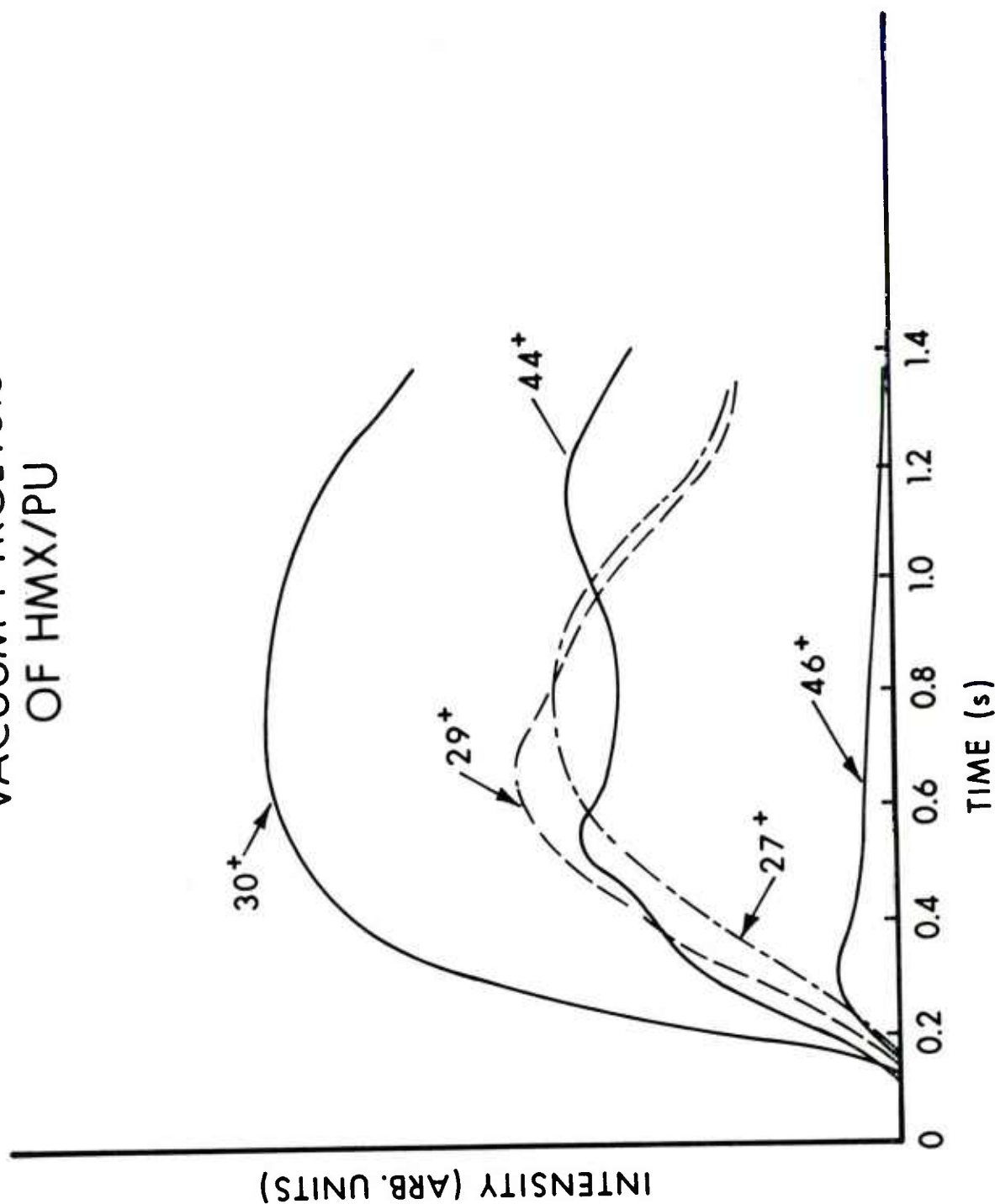
Figure 6. Rapid Pyrolysis Behavior of HMX/PU. Mass/Charge Peaks not Identified in Figure 5 are HCH (27), NO_2 (46), and CO_4 (44)

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may either be due to gas phase chemistry due to higher temperatures of the products, or may be a result of the binder pyrolysis lagging behind that of the HMX. In most cases, approximately constant relative concentrations of these major species are observed at early times in these preliminary measurements.

To obtain preliminary relative quantitative values for the major stable species data were acquired using the sample/hold system recorded by an oscilloscope and film. Calibration of the system was performed by using NO_2, NO, and N_2O gases and by heating paraformaladehyde in the pyrolysis chamber to form HCHO. Purity of the nitrogen oxides was checked via infrared absorption spectroscopy. The analog scanner was used to monitor the mass spectrum during paraformaldehyde heating to verify that HCHO was the principal gas phase molecule evolved after initial degassing. Calibrations were performed over the pressures of the data acquisition; pressures were measured with a capacitance manometer. The calibration voltages were read on a digital voltmeter to reduce error. These values were then used to reduce the numbers measured from the film to absolute pressures of the species at the chosen time. The numbers quoted in Table I are the average of six runs where measurements were made shortly before the peak signal recorded in each case. As can be seen in the table, the dominant species is N_2O with substantial quantities of NO_2, HCN, and HCHO also produced. In Table II are listed the species and signal strengths from oscilloscope raster scans made under similar conditions. Note that the signal intensity is only indirectly related to actual concentration due to cross section and fragmentation pattern variations when the species are ionized in the electron impact region. The interpretation of these data for the understanding of the mechanism of thermal decomposition of HMX is discussed below.

IV. DISCUSSION OF RESULTS

The absence of a substantial heating rate effect in the pyrolysis of HMX/PU over the limited range of variation of these studies may be due to several factors. It is possible that the heating rate is already sufficiently high that variations in it are no longer important. A second possibility is that the sample absorbs the laser light in an extremely thin surface layer, resulting in the removal of the pyrolyzed layer without substantial interaction with the remaining solid. Thus one must have information about the relative optical densities and depth of absorption of the light before comparing observed behavior of two different materials such as NC and HMX/PU. It is certainly more likely that one will observe heating rate effects in heating solids with filaments since the removal of gaseous species from the surface is necessarily slower, except as the material thickness becomes extremely small. It is probably most correct to interpret the data presented here as related to the primary decomposition products, whereas filament pyrolysis, especially at higher pressure, produces a mixture of primary and secondary products when the species are highly reactive.

Table I. Relative Intensities of Major Pyrolysis Products from HMX/PU

Species	Concentration
N_2O	100
NO_2	54
HCN	42
HCHO	39
NO	27

Table II. Species Observed in Pyrolysis of HMX/PU

m/e	Signal Intensity[a]	Identification
14	w	CH_2, N
15	w	CH_3, NH
16	w	O, NH_2
17	w	OH
18	m	H_2O
26	m	CN
27	ms	HCN
28	s	CO, N_2
29	s	CHO
30	s	H_2CO, NO
41	mw	*
42	mw	*, CNO
43	mw	*
44	s	N_2O, CO_2
46	ms	NO_2
47	w	HONO
55-60	w	*
70	w	*

[a] w=weak, m=medium, s=strong

* ring fragments

The presence of N_2O and HCHO among the decomposition products of nitramines has been known since the earliest studies[4]. Through the use of isotopic labeling of the nitro-N, Suryanarayana et al[5] were able to show in a study of thermal decomposition followed by mass spectroscopy that the N-N bond is not broken in going from HMX to N_2O. This result has led them to propose a concerted decomposition mechanism which may be written as

$$HMX \rightarrow 4[CH_2-N-NO_2] \rightarrow 4N_2O + 4HCHO$$
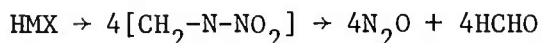
with an oxadiazol intermediate. This mechanism was also proposed in essence by Robertson[4] although without the support of the isotope labeling results. Although the idea of a concerted mechanism is probably not generally accepted[6], current discussions in the community of nitramine research often imply that N_2O/HCHO chemistry is dominant in the understanding of ignition and combustion of these materials.

Thermochemical studies[7], as well as chemical intuition, suggest that since it is the weakest bond the $N-NO_2$ bond should be the first to break. This step would then be followed by ring breakup and further chemistry. The amounts of NO_2 and the presence of ring fragments as observed in our studies strongly support this mechanism and suggest that some of the earlier studies[4,5] are misleading due to the possibility of substantial reactions between the primary decomposition species before any measurements are made. The N_2O could result from the further reactions of the ring fragments, in agreement with the findings of Suryanarayana et al[5].

[4] A. J. B. Robertson, "The Thermal Decomposition of Explosives: Part II. Cyclotrimethylenetrinitramine and Cyclotetramethylenetetranitramine", Trans. Faraday Soc. (Part 1), 45, 85-93 (1949).

[5]
a. B. Suryanarayana, R. J. Graybush, and J. R. Autera, "Thermal Degradation of Secondary Nitramines: A Nitrogen-15 Tracer Study of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane)", Chem. and Ind. p 2177 (1967).
b. B. Suryanarayana and R. J. Graybush, "Thermal Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX): A Mass Spectrometric Study of the Products from β-HMX", Proc. of the 39th Cong. on Ind. Chem., Brussels, Belgium (1966).
c. B. Suryanarayana, J. R. Autera, and R. J. Graybush, "Mechanism of Thermal Decomposition of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX)", Proc. of the 1968 Army Sci. Conf. (OCRD), West Point, NY, 2, 423 (1968).

[6] K. P. McCarty, "HMX Propellant Combustion Studies", AFRPL-TR-76-59, AD #B017527, 9-12 (1976).

[7] R. Shaw, "Estimated Kinetics and Thermochemistry of Some Initial Unimolecular Reactions in the Thermal Decomposition of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane) in the Gas Phase", J. Phys. Chem. (in press).

Preliminary studies with infrared absorption spectroscopy detection of the product species verify that the laser method of heating is not causing substantially enhanced $N-NO_2$ bond breaking as compared to rapid heating of a hot pyrex vessel containing HMX or RDX. This work also indicates that the binder is not causing a major change in the relative amount of NO_2 produced in decomposition of HMX/PU compared to that of HMX. These results will be published separately upon completion.

V. CONCLUSIONS

The data acquisition system for the time-of-flight mass spectrometer used with the molecular beam sampling facility has been described in detail. The oscilloscope intensification raster display method has been substantially improved upon with the use of positive/negative film and microdensitometer scanning of the negative. This technique allows one to record semi-quantitative time resolved data for the entire mass spectrum with good time resolution. A wide-band sample-and-hold system has been designed and assembled which allows acquisition of temporal behavior of at least four masses with reproducibility, ease of calibration, and good time resolution.

Pyrolysis of NC and HMX/PU has been studied using CO_2 laser heating and rapid sampling and analysis of the resulting chemical species. These studies indicate that there is no heating rate effect for the pyrolysis of HMX/PU under the conditions of these experiments. The chemical species observed support a decomposition mechanism for HMX which involves breaking of the $N-NO_2$ bond as the primary step. These results are in agreement with chemical intuition and recent thermochemical calculations.

REFERENCES

1. a. J. W. Hastie, "Sampling Reactive Species From Flames by Mass
        Spectrometry", Int. J. of Mass Spectry and Ion Physics, 16,
        89-100 (1975).

    b. R. V. Serauskas, G. R. Brown, and R. Pertel, "A Supersonic
        Molecular Beam Atmospheric Pressure Flame Sampling System",
        Int. J. of Mass Spectry and Ion Physics, 16, 69-87 (1975).

    c. J. C. Biordi, C. P. Lazzara, and F. J. Papp, "Flame-Structure
        Studies of CF_3Br-Inhibited Methane Flames", Symp. (Int.)
        Comb. (Proc.), 14th, 367 (1973).

2. K. J. White and R. W. Reynolds, "Apparatus for Detecting Interior
    Ballistic Combustion Products", BRL Memorandum Report No. 2497,
    AD #A013372 (1975).

3. K. A. Lincoln, Rev. Sci. Instr., 35, 1688 (1964).

4. A. J. B. Robertson, "The Thermal Decomposition of Explosives:
    Part II. Cyclotrimethylenetrinitramine and Cyclotetramethylene-
    tetranitramine", Trans. Faraday Soc. (Part 1), 45, 85-93 (1949).

5. a. B. Suryanarayana, R. J. Graybush, and J. R. Autera, "Thermal
        Degradation of Secondary Nitramines: A Nitrogen-15 Tracer
        Study of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane),"
        Chem. and Ind., p 2177 (1967).

    b. B. Suryanarayana and R. J. Graybush, "Thermal Decomposition of
        1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX): A Mass
        Spectrometric Study of the Products from β-HMX", Proc. of
        the 39th Cong. on Ind. Chem., Brussels, Belgium (1966).
    c. B. Suryanarayana, J. R. Autera, and R. J. Graybush, "Mechanism
        of Thermal Decomposition of HMX (1,3,5,7- ...)", Proc. of the
        1968 Army Science Conf. (OCRD), West Point, NY, 2, 423 (1968).

6. K. P. McCarty, "HMX Propellant Combustion Studies", AFRPL-TR-76-59,
    AD #B017527, 9-12 (1976).

7. R. Shaw, "Estimated Kinetics and Thermochemistry of Some Initial
    Unimolecular Reactions in the Thermal Decomposition of HMX (1,3,5,
    7-Tetranitro-1,3,5,7-Tetrazacyclooctane) in the Gas Phase", J.
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